PATENT SPECIFICATION

781,255

Date of Application and filing Complete Specification: April 25, 1956.

No. 12631/56.

Application made in Switzerland on April 27, 1955.

Complete Specification Published: Aug. 14, 1957.

Index at acceptance:—Class 2(3), C2B37(A1: K).

International Classification:—C07c.

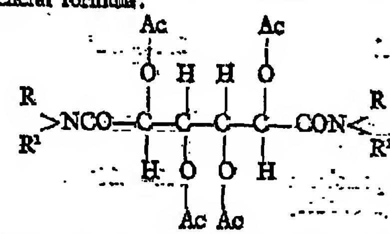
COMPLETE SPECIFICATION

Process for the Production of New Derivatives of Mucic Acid

We, J. R. GEIGY A.-G., a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with new derivatives of mucic acid which have valuable pharmacological properties, as well as a process for the production thereof.

Diamides of tetra-acetyl mucic acid of the general formula:



I

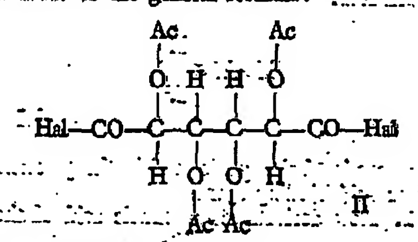
wherein R represents an aliphatic hydrocarbon radical containing at most 5 carbon atoms,

R^1 represents hydrogen or an aliphatic hydrocarbon radical containing at most 5 carbon atoms,

and Ac is an abbreviation for the acetyl radical CH_3—CO—, have not been known up to now.

It has now been found that such compounds have a strong antiphlogistic action.

The new mucic acid derivatives defined above can be produced in a simple manner by reacting 1 mol of tetra-acetyl mucic acid dihalide of the general formula:



II

wherein Hal represents chlorine or bromine, with 2 mols of amines of the general formula:

$$H—N<\begin{matrix}R\\R^1\end{matrix} \qquad \text{III}$$

wherein R and R^1 have the meanings given above, the reaction being performed in the presence of an acid binding agent. For example, an excess of the amine used can be the acid binding agent and the reaction can be performed in a suitable inert organic solvent or diluent, *e.g.* in benzene, in the warm. Examples of amines of the general formula III are: methylamine, ethylamine, *n*-propylamine, isopropylamine, *n*-butylamine, *sec.* butylamine, *iso*butylamine, *n*-amylamine, *iso*amylamine, allylamine, methallylamine, dimethylamine, diethylamine, *di-n*-propylamine, di-*n*-butylamine, di-*iso*butylamine, diallylamine, dimethallylamine, methyl-ethylamine, methyl-*n*-propylamine, methyl-isopropylamine, methyl-*n*-butylamine, methyl-*iso*-butylamine, methyl-amylamine, methyl-*iso*amylamine, methyl-allylamine, methyl-methallylamine, and ethyl-allylamine.

Tetra-acetyl mucic acid dichloride can be obtained from tetra-acetyl mucic acid (Skraup, *Monatshefte für Chemie 14*, 488) for example by means of phosphorus pentachloride (Diels, Löflund, Berichte der deutsch. chem. Gesellschaft, *47*, 2352 (1914)) or by means of thionyl chloride (J. Müller, Berichte der deutsch. chem. Gesellschaft *47*, 2655).

The following examples serve to illustrate the production of the new compounds. Parts are given as parts by weight unless otherwise indicated and their relationship to parts by volume is as that of grammes to cubic centimetres. The temperatures are in degrees Centigrade.

EXAMPLE 1

13.5 Parts of tetra-acetyl mucic acid dichloride are suspended in 200 parts by volume of abs. benzene and, while stirring and cooling with water, 11 parts of diethyl-

amine in 50 parts by volume of abs. benzene are added dropwise at 30—35°. On completion of the dropwise addition, the whole is boiled under reflux for 2 hours. After cooling, about 100 parts by volume of 2 N-hydrochloric acid are added and the precipitated tetra-acetyl mucic acid-bis-diethylamide is filtered off under suction. This is then washed with saturated aqueous bicarbonate solution and water. Recrystallised from ethyl acetate, it melts at 194—195°.

EXAMPLE 2

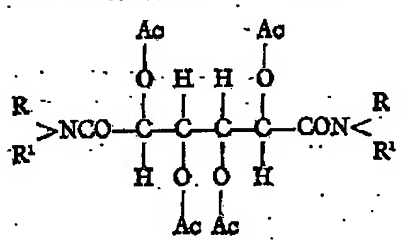
13.5 Parts of tetra-acetyl mucic acid dichloride in 200 parts by volume of abs. benzene are reacted as described above with 18 parts of di-*n*-butylamine. After cooling, the benzene solution in the separating funnel is washed with 2 N-hydrochloric acid, saturated bicarbonate solution and water. After drying with sodium sulphate, the benzene is distilled off and the residue is recrystallised from ethyl acetate. The tetra-acetyl mucic acid bis-di-*n*-butylamide so obtained melts at 162—163°.

The following compounds of the general formula I for example, are obtained in an analogous manner:

R	R^1	recrystallised from	M.P.
$CH_3—$	$CH_3—$	ethanol	229—230°
$CH_3CH_2—$	H—	methanol	310—312° on decomposition
$CH_3—CH_2—CH_2—$	$CH_3—CH_2—CH_2—$	ethyl acetate	188—189°
$\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH_2—$	$\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH_2—$	methanol	168—169°
$\begin{matrix}CH_3\\CH_3\end{matrix}\geq C—CH_2—$	$\begin{matrix}CH_3\\CH_3\end{matrix}>C—CH_2—$	ethanol	170—171°
$n—C_4H_9$	H—	methanol	232—233°
$CH_3—$	$n—C_4H_9$	ether/petroleum ether (about 1:1)	111—112°

What we claim is:—

1. Process for the production of new derivatives of mucic acid of the general formula:

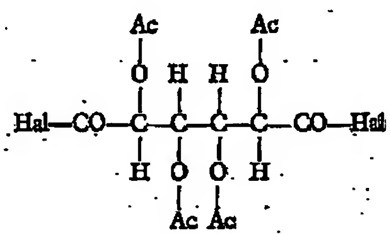


I

wherein R represents an aliphatic hydrocarbon radical containing at most 5 carbon atoms,

R^1 represents hydrogen or an aliphatic hydrocarbon radical containing at most 5 carbon atoms, and

Ac represents the acetyl radical $CH_3—CO—$, which comprises reacting one mol of a tetra-acetyl mucic acid dihalide of the general formula:



II

wherein Hal represents chlorine or bromine and Ac has the meaning defined above, with 2 mols of an amine of the general formula:

$$H—N<\begin{matrix}R\\R^1\end{matrix} \qquad \text{III}$$

the reaction being performed in the presence of an acid binding agent.

2. New derivatives of mucic acid of the

formula I given in claim 1 wherein R, R^1 and Ac have the meanings given in claim 1.

3. Process for the production of new derivatives of mucic acid substantially as herein described with reference to and as illustrated in any of the foregoing examples.

4. Derivatives of mucic acid herein particularly described in any of the foregoing examples.

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12, Church Street, Liverpool, 1,
Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1957.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 September 2002 (12.09.2002)

PCT

(10) International Publication Number
WO 02/070463 A1

(51) International Patent Classification[7]: C07C 235/06, 235/14

(21) International Application Number: PCT/NL02/00151

(22) International Filing Date: 6 March 2002 (06.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01200836.3 6 March 2001 (06.03.2001) EP

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(81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), DE (utility model), DK (utility model), DM, DZ, EC, EE (utility model), ES, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/070463 A1

(54) Title: GELLING AGENTS OR THICKENERS

(57) Abstract: The invention relates to novel class of gelling agents or thickeners, to a process for preparing said gelling agents or thickeners and to their use to prepare gels. The present gelling agents or thickeners have the form of a N,N'-disubstituted aldaramide or N,N'-disubstituted pentaramide.

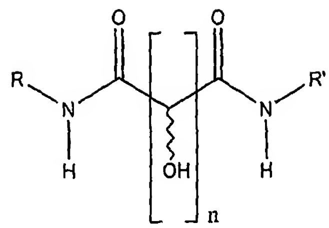
Title: Gelling agents or thickeners

The invention relates to a novel class of gelling agents, a process for producing them and to their application in preparing gels for various applications.

Thermally reversible gelling or thickening of organic solvents by low molecular weight compounds are of particular interest for hardeners of spilled fluids and cooking oils, thickeners for paints, cosmetic materials and several other technical applications. The self assembly of these gelator/thickener molecules occurs by means of non-covalent interactions such as hydrophobic interaction, π-π interactions, electronic interactions, hydrogen bonding or combinations thereof. Although several gelator/thickener molecules have been identified during the last decade, there is still interest in stable gelator/thickeners that can be synthesized easily from cheap, renewable sources and gelate or thicken a wide variety of solvents.

The present invention aims to provide a novel class of gelling agents or thickeners. It is an object of the invention to provide gelling agents or thickeners that are based on readily available and economically attractive starting materials. It is further an object of the invention to provide gelling agents or thickeners that are capable of gelling or thickening a wide variety of solvents making the gelling agents or thickeners suitable to be employed in various applications. Other objects of the invention will become clear from the discussion of the invention and a number of its embodiments presented below.

Surprisingly, it has been found that the above objects can be reached by preparing gelling agents or thickeners from low molecular carbohydrates. The present invention relates to a gelling agent in the form of a N,N'-disubstituted aldaramides and N,N'-disubstituted pentaramides and derivatives thereof. Specifically, the invention relates to a gelling agent having the following structure



(I),

wherein n is 3 or 4, and wherein R and R' represent the same or different substituents chosen from the group of substituted or unsubstituted, branched, possibly aromatic groups containing, cyclic or linear alkyl, alkenyl, alkynyl groups having from 1 to 40 carbon atoms. In a preferred embodiment, R and R' each represent independently a linear, branched, or cyclic alkyl group having 4-20 carbon atoms. More preferred is that R and R' each are independently selected from the group of cycloalkyl groups having 4-16 carbon atoms. In a preferred embodiment, R and R' represent the same substituent.

It is one of the advantages of the present gelling agents or thickeners can be based on naturally occurring products, such as carbohydrates. Thus, the starting materials for producing them are from a renewable source.

A gelling agent or thickener according to the invention may be prepared by converting an aldose or pentose to its corresponding aldaric or pentaric acid, or a salt thereof, such as an alkali metal salt or an (alkyl)ammonium salt. It is preferred to use an aldose or pentose chosen from the group of allose, altrose, glucose, mannose, gulose, idose, galactose, talose, ribose, arabinose, xylose, lyxose and derivatives thereof, as these lead to products having particularly favorable gelling and/or thickening properties. It is to be noted that both the L and the D isomers of the aldose or pentose, as well as mixtures thereof, can be used. Suitable derivatives of the mentioned aldoses and pentoses include deoxy aldoses or pentoses, ethers, esters and the like. In a more preferred embodiment, D-glucose is chosen as aldose.

The conversion of the aldose or pentose to its corresponding aldaric or pentaric acid is generally achieved by oxidation. The oxidation can suitably

be carried out using Pt/O_2,TEMPO/NaOCl/(NaBr) or HNO_3/($NaNO_2$) as an oxidizing agent. Further details for the manner in which the oxidation may be carried out can be found in US patents 5,831,043, 5,599,977 and 6,049,004, and in J. Org. Chem., 1977, 42, 3562-3567; J-F. Thaburet *et al.*, Carbohydr. Res. 330 (2001), 21-29, all of which are incorporated herein by reference.

The thus obtained aldaric or pentaric acid or salt thereof is subsequently condensed with a primary amine to obtain the objective gelling agent or thickener.

The aldaric or pentaric acid can be condensed with an amount of at least 200 mole%, with respect to the aldaric or pentaric acid, of a primary amine. It is preferred to activate the aldaric or pentaric acid first by means of lactonization and/or esterification, depending on the stereochemistry of the carbohydrate. Further details may be found in Kurtz et al., J. Biol. Chem., 1939, 693-699; Hoagland, Carbohydrate Res., 1981, 98, 203-208, and US patent 5,312,967, which are incorporated herein by reference.

In an alternative embodiment, non-symmetrical N,N'-dialkylaldaramides or N,N'-dialkylpentaramides may be prepared, wherein R and R' represent different substituents. In accordance with this embodiment, the aldaric or pentaric acid may be converted into an N-alkyl-1-aldar/pentaramid-6-ate or N-alkyl-6-aldar/pentaramid-1-ate (as disclosed in US patent 5,239,044; L. Chen *et al.*, J. Org. Chem., 61 (1996) 5847-5851; R. Lee *et al.*, Carbohydr. Res. 64 (1978) 302-308; and K. Hashimoto *et al.*, J. Polym. Sci. Part A, Polym. Chem., 37 (1999) 303-312), activated, and subsequently condensed with, preferably 100 mole% with respect to the N-alkyl aldar/pentar-ate, of a second primary amine.

In general, the obtained gelling agent or thickener precipitates from the reaction mixture in which it is formed and can be easily isolated by filtration. Further purification can be performed by conventional techniques like crystallization or, in the case of products based on galactaric acid derivatives, by thoroughly washing with ethanol, water, acetone or hexane.

It will be understood that the use of the present gelling agents or thickeners to prepare a gel or to thicken a composition is also encompassed by the invention. As is well-known, gelling behavior of compounds or compositions is highly unpredictable. In principle, a solution of a specific compound in a solvent, e.g. an organic solvent, is considered a gel when a homogeneous substance is obtained which exhibits essentially no gravitational flow. Preferably, the gelling phenomenon is thermoreversible. However, in as far as the present compounds do not provide a gel in a composition, they may be used as a thickener or rheology controlling agent as their addition to a composition may give rise to an increase in viscosity of the composition.

Compositions in which the present compound have been found to produce a gel include compositions in numerous solvents. Preferred examples include aromatic and non-aromatic hydrocarbons, alcohols, ethers, esters, aldehydes, alkanoic acids, epoxides, amines, halogenated hydrocarbons, silicon oils, vegetable oils, phosphoric esters, sulfoxides, water and mixtures thereof. In order to obtain a gel, the gelling agent or thickener is preferably mixed with the composition to be transformed to a gel in an amount of between 0.01 and 50 wt.%, based on the weight of the composition. In a preferred embodiment the mixture of the gelling agent or thickener and the composition is heated to allow for an even better gel formation or thickening. Typically, the heating will involve raising the temperature of the mixture to about 30 - 175 °C until a clear solution is obtained. In an alternative embodiment, the gelling agent is first dissolved in a polar or apolar solvent and then added to or sprayed into a composition or solvent to be converted into a gel.

The resultant gel or thickened composition, which is also encompassed by the present invention, may find use in one of numerous applications. It is conceived that such applications lie in the field of cosmetics, oil recovery (*e.g.* from the sea), food products, transport of industrial solvents, stabilization of organic solvents under near zero gravity conditions, stiffening of fuels to increase stability and reduce fluidity, lubricants, coatings, printing

inks, and adhesives. In these applications they may be used analogous to conventional gelling agents or thickeners, which they replace.

The invention will now be further elucidated by the following, non-restrictive examples.

EXAMPLES

Synthesis of starting materials

Potassium hydrogen D-glucarate (R.L. Whistler, M.L. Wolfrom, J.N. BeMiller, *Methods in Carbohydrate Chemistry*, Vol II (1963), Academic Press Inc, 47-48), D-glucaric acid (lactone) (L. Chen, D.E. Kiely, *J. Org. Chem.*, 61 (1996) 5847-5851), D-glucaro-6,3-lactone (L. Chen, D.E. Kiely, *J. Org. Chem.*, 61 (1996) 5847-5851), D-mannaric acid dilactone (E. Fischer, Berichte, 24 (1891) 539-546), diethyl galacterate (R.L. Whistler, M.L. Wolfrom, J.N. BeMiller, *Methods in Carbohydrate Chemistry*, Vol II (1963) Academic Press Inc, 40-41), D-ribaric acid (lacton) (C.E. Cantrell, D.E. Kiely, G.J. Abruscato, J.M. Riordan, *J. Org. Chem.*, 42 (1977) 3562-3567, as described for D-xylaric acid, R.E. Gall, L. Tarasoff, *Aust. J. Chem.*, 28 (1975) 687-691) were synthesized according to literature procedures.

Cyclohexylammonium 6-(N-cyclohexyl)-D-glucaramide-1-ate.

D-glucaro 6,3-lacton (1.04 g, 5.4 mmol) was added to a solution of cyclohexylamine (1.34 g, 13.5 mmol) in EtOH (50 ml). After 20 stirring the precipitate was filtered off and crystallized from EtOH. Yield 0.97 g, (2.5 mmol, 46%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm, δ 1.10-1.38 (m, 10 H), 1.45-1.90 (m, 10H), 2.91 (m, 1H), 3.55 (m, 1H), 3.65 (m, 2H), 3.78 (t, 1H), 3.89 (d, 1H), 7.55 (d, 1H). ^{13}C-NMR (d6-DMSO, 300 MHz, ppm): 24.54, 25.23, 25.32, 25.85, 31.28, 32.86, 32.93, 47.88, 49.82, 71.60, 72.45, 72.80, 73.27, 172.70,

176.36. Anal Calcd for $C_{18}H_{34}N_2O_7$: C, 55.37; H, 8.78, N, 7.17. Found: C, 55.22; H, 8.76; N, 7.37.

Synthesis of 3-O-methyl diethyl D-glucaric acid.

3-*O*-Methyl-∀,∃-D-glucose (7.00 g, 36 mmol) was added in portions (in 45 minutes) to a solution of $NaNO_2$ (0.010 g, 0.14 mmol) in HNO_3 (15 ml, 65%) at T = 50-55° C. After 45 minutes T = 50° C the reaction was cooled to RT, and stirred for another 30 minutes. EtOH (40 ml) was added in portions and the reaction mixture was stripped with EtOH several times using a rotavap. The crude reaction mixture was distilled (Kugelrohr) and the fraction of b.p. 225° C/0.4 mm Hg was collected. Yield 4.74 g (16.9 mmol, 47%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm, δ 1.20 (t, 6H), 3.31 (s, 3H), 4.10 (m, 4H + 1H), 4.35 (m, 1H), 4.49 (m, 1H), 4.94 (t, 1H). ^{13}C-NMR (d_6-DMSO, 300 MHz, ppm): 15.09, 59.50, 61.47, 69.96, 71.81, 78.06, 83.89, 171.47, 176.02.

Synthesis of citronellylamine.

1) Preparation of 3,7-dimethyl-oct-6-enal oxim. Citronellal (15,37 g, 100 mmol) in EtOH (300 ml) was added to a solution of NH_2OH (7.00 g, 100 mmol) and NaOH (4.07 g, 102 mmol) in H_2O (100 ml) and stirred for 20 hours at T = 60° C. After evaporation the remaning oil was dissolved in H_2O, acidified with 2M HCl, and subsequently extracted with Et_2O (2 x). After drying with Na_2SO_4 filtration and evaporation crude 3,7-dimethyloct-6-enal oxim (mixture of cis/trans) was isolated. Yield 14.89 g (88 mmol, 88%). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm, δ 0.88 (t, 3H), 1.11-1.34 (m, 2H), 1.54 (s, 3H), 1.62 (s, 3H), 1.94-2.30 (m, 5H), 5.01 (t, 1H), 6.69 (t, 0.5 H), 7.36 (0.5 H). ^{13}C-NMR ($CDCl_3$, 300 MHz, ppm): 15.12, 16.92, 17.21, 22,89, 22.95, 23.18, 27.98, 28.42, 29.47, 33.88, 34.11, 34.32, 121.79, 121.84, 128.96, 148.91. 2) Preparation of citronellyl amine. 3,7-Dimethyloct-6-enal oxim (mixture of cis/trans 1:1, 14.54 g, 68 mmol) was added slowly to 173 ml of a solution of 1M $LiAlH_4$ in THF under N_2 atmosphere. After 20 hours refluxing the suspension

was decanted and the precipitate was washed with Et_2O (3x). After drying of the Et_2O/THF layer with Na_2SO_4, filtration and evaporation of the solvent the remaining oil was distilled under reduced pressure (0.8-1.0 mm Hg, T = 65° C). Yield 5.00 g (32.4 mmol, 37%). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm, δ 0.88 (d, 3H), 0.92-1.44 (m, 7H), 1.50 (s, 3H), 1.58 (s, 3H), 1.88 (m, 2H), 2.62 (m, 2H), 5.00 (t, 1H). ^{13}C-NMR ($CDCl_3$, 300 MHz, ppm): 15.07, 17.00, 22.94, 23.15, 27.57, 34.67, 37.57, 38.68, 122.27, 128.57.

Synthesis of 8-amino-pentadecane.

1) Preparation of pentadecan-8-one oxim. Dihexylketon (13,47 g, 68 mmol) in EtOH (300 ml) is added to a solution of NH_2OH (4.74 g, 68 mmol) and NaOH (2.74 g, 69 mmol) in H_2O (100 ml) and stirred for 20 hours at T = 60° C. After evaporation the remaning oil is dissolved in H_2O, acidified with 2M HCl, and subsequently extracted with Et_2O (2 x). After drying with Na_2SO_4 filtration and evaporation crude pentadecan-8-one oxim (mixture of cis/trans 1:1) was isolated. Yield 13.57 g (64 mmol, 93%). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm, δ 0.83 (t, 6H), 1.25 (m, 8H), 1.45 (m, 4H), 2.11 (t, 2H), 2.28 (t, 2H). ^{13}C-NMR ($CDCl_3$, 300 MHz, ppm): 11.56, 20.06, 23.13, 23.76, 25.99, 26.51, 27.07, 29.09, 31.61, 159.57. 2) Preparation of 8-amino-pentadecane. Pentadecan-8-one oxim (mixture of cis/trans 1:1, 13.45 g, 63 mmol) was added slowly to 127 ml of a solution of 1M $LiAlH_4$ in THF under N_2 atmosphere. After 20 hours refluxing the suspension was decanted and the precipitate was washed with Et_2O (3x). After drying of the Et_2O/THF layer with Na_2SO_4, filtration and evaporation of the solvent the remaining oil was distilled under reduced pressure (0.8-1.0 mm Hg, T = 105° C). Yield 5.17 g (26.1 mmol, 41%). %). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm, δ 0.79 (d, 6H), 1.18-1.30 (m, 20H), 2.58 (m, 1H). ^{13}C-NMR ($CDCl_3$, 300 MHz, ppm): 11.53, 20.09, 23.62, 26.97, 29.35, 35.67, 48.67.

Example 1

Synthesis of dibutyl D-glucaramide. D-Glucaric acid (lactone) (1.43 g, about 7.1 mmol) was added to a solution of butylamine (1.34 g, 17.9 mmol) in EtOH (30 ml). After 20 hours stirring the precipitate was filtered off and crystallized from EtOH (yield 0.31 g, 1.0 mmol, 14%).^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 0.87 (t, 6H), 1.28 (m, 4H), 1.40 (m, 4H), 3.08 (m, 4H), 3.69 (bs, 1H, H_4), 3.88 (bs, 1H, H_3), 3.92 (bs, 1H, H_5), 3.98 (bs, 1H, H_2), 4.61 (d, 1H, OH_3), 4.74 (d, 1H, OH_4), 5.35 (d, 1H, OH_2), 5.52 (d, 1H, OH_5), 7.59 (t, 1H, NH_1), 7.84 (t, 1H, NH_6). ^{13}C-NMR (d6-DMSO, 300 MHz, ppm): 14.65, 20.45, 32.21, 38.83, 71.33, 72.50, 73.95, 74.21, 173.01, 173.98, Anal Calcd for $C_{14}H_{28}N_2O_6$: C, 52.48; H, 8.81, N, 8.74. Found: C, 52.06; H, 8.79; N, 8.61.

Example 2

Synthesis of dibutyl D-mannaramide. D-Mannaric acid dilactone (0.61 g, 3.5 mmol) is added to a solution of butylamine (0.81 g, 10.8 mmol) in EtOH (20 ml). After 20 hours stirring the precipitate was filtered off and crystallized from EtOH (yield 0.38 g, 1.2 mmol, 34%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 0.87 (t, 6H), 1.24 (m, 4H), 1.39 (m, 4H), 3.09 (q, 4H), 3.70 (t, 2H, H_3, H_4), 3.88 (t, 2H, H_2, H_5), 4.79 (d, 2H, OH_3, OH_4), 5.42 (d, 2H, OH_2, OH_5), 7.84 (t, 2H, NH_1, NH_6). ^{13}C-NMR (d_6-DMSO, 300 MHz, ppm): 14.64, 20.45, 32.13, 38.59, 72.09, 72.37, 174.36. Anal Calcd for $C_{14}H_{28}N_2O_6$: C, 52.48; H, 8.81, N, 8.74. Found: C, 52.07; H, 8.79; N, 8.65.

Example 3

Synthesis of dibutyl galactaramide. Diethyl Galactarate (2.00 g, 7.5 mmol) was added to a solution of butylamine (1.40 g, 18.8 mmol) in EtOH (30 ml). After 20 hours stirring the precipitate was filtered off and crystallized from DMSO/H_2O (yield 0.30 g, 0.9 mmol, 13%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 0.88 (t, 6H), 1.29 (m, 4H), 1.40 (m, 4H), 3.11 (m, 4H), 3.78 (s, 2H, H_3, H_4), 4.11 (s, 2H, H_2, H_5), 4.39 (bs, 2H, OH_3, OH_4), 5.23 (bs, 2H, OH_2, OH_5), 7.55

(t, 2H, NH_1, NH_6). ^{13}C-NMR (d_6-DMSO, 300 MHz, ppm): 14.67, 20.41, 32.32, 38.86, 71.57, 174.07. Anal Calcd for $C_{14}H_{28}N_2O_6$: C, 52.48; H, 8.81, N, 8.74. Found: C, 51.58; H, 8.88; N, 8.50.

Example 4

Synthesis of dicyclohexyl D-ribaramide. D-Ribaric acid (lacton) (0.32 g, 2.0 mmol) was added to a solution of NEt_3 (0.25 ml) and cyclohexylamine (0.45 g, 4.5 mmol) in EtOH (20 ml). After 20 h stirring the solution was cooled to T = 4° C and filtered. Yield 0.14 g (0.41 mmol, 20%). ^{1}H-NMR (d_6-DMSO, 500 MHz, T = 100° C, ppm): δ 1.27(m, 10H), 1.70 (m, 10H), 3.59 (bs, HDO + 1H), 3.97 (s, 2H), 7.52 (d, 1H, NH_6). ^{13}C-NMR (d_6-DMSO, 300 MHz, ppm): 25.90, 26.38, 33.42, 48.59, 73.24, 75.98, 173.12. Anal Calcd for $C_{17}H_{30}N_2O_5$: C, 59.63; H, 8.83, N, 8.18. Found: C, 59.30; H, 9.05; N, 8.03.

Example 5

Synthesis of dicyclohexyl D-glucaramide. D-Glucaro 6,3 lactone (1.07 g, 5.6 mmol) was added to a solution of p-toluene sulfonic acid (0.042 g, 0.22 mmol) in EtOH (20 ml). At T = 50°C cyclohexylamine (1.10 g, 11,1 mmol) is dropped slowly to the solution. After 1 h stirring the solution was cooled to RT and H_2O (20 ml) was added. Evaporation till 10-15 ml gave a white precipitate which was filtered off and crystallized from EtOH (yield 0.89 g, 2.1 mmol, 38%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 1.26 (m, 10H), 1.69 (m, 10H), 3.56 (bs, 2H), 3.68 (bs, 1H), 3.89 (bs, 2H), 3.96 (s, 1H), 4.61 (d, 1H), 4.69 (d, 1H), 5.36 (d, 1H), 5.45 (d, 1H), 7.31 (d, 1H, NH_1), 7.58 (d, 1H, NH_6). ^{13}C-NMR (d6-DMSO, 300 MHz, ppm): 25.57, 26.07, 33.16, 48.10, 48.25, 71.34, 72.57, 73.85, 74.04, 172.17, 172.98, Anal Calcd for $C_{18}H_{32}N_2O_6$: C, 58.05; H, 8.66, N, 7.52. Found: C, 58.11; H, 8.76; N, 7.46.

Example 6

Synthesis of dicyclohexyl D-mannaramide. D-Mannaric acid dilactone (0.45 g, 2.3 mmol) was added to a solution of cyclohexylamine (0.58 g, 5.9 mmol) in EtOH (20 ml). After 20 hours stirring the solution was refluxed for 2 hours and after cooling the precipitate was filtered off and crystallized from EtOH (yield 0.05 g, 0.13 mmol, 6%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 1.24 (m, 10H), 1.70 (m, 10H), 3.59 (bs, 2H), 3.69 (t, 2H), 3.86 (t, 2H), 4.72 (d, 2H), 5.34 (d, 2H), 7.62 (d, 2H, NH). ^{13}C-NMR (d_6-DMSO, 300 MHz, ppm): 25.52, 26.10, 33.16, 48.26, 71.96, 72.27, 173.36. Anal Calcd for $C_{14}H_{28}N_2O_6$: C, 58.05; H, 8.66, N, 7.52. Found: C, 57.80; H, 8.74; N, 7.37.

Example 7

Synthesis of dicyclohexyl galactaramide. Diethyl galacterate (2.66 g, 10.0 mmol) was added to a solution of cyclohexylamine (2.68 g, 27.0 mmol) in EtOH (50 ml). After 20 hours stirring the suspension was refluxed for 3 hours and after cooling the precipitate was filtered off, washed with H_2O/aceton 9:1 (3 x 25 ml) and H_2O (50 ml) and crystallized from DMSO (yield 0.84 g, 2.3 mmol, 23%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 1.24 (m, 10H), 1.71 (m, 10H), 3.60 (bs, 2H), 3.76 (d, 2H), 4.09 (d, 2H), 4.38 (d, 2H), 5.18 (d, 2H), 7.26 (d, 2H, NH). ^{13}C-NMR (d_6-DMSO, 300 MHz, ppm): 25.08, 25.82, 32.95, 47.87, 71.39, 71.60, 172.74. Anal Calcd for $C_{14}H_{28}N_2O_6$: C, 58.05; H, 8.66, N, 7.52. Found: C, 57.88; H, 8.74; N, 7.42.

Example 8

Synthesis of dioctyl D-glucaramide. D-Glucaric acid (lactone) (1.35 g, about 7.0 mmol) was added to a solution of octylamine (1.85 g, 14.0 mol) in EtOH (30 ml). After 20 hours stirring the suspension was refluxed for 3 hours and after cooling the precipitate was filtered off and recrystallized twice from EtOH (yield 0.57 g, 1.3 mmol, 19%). ^{1}H-NMR (d_6-DMSO, 500 MHz, COSY, T = 50°C, ppm): δ 0.83 (t, 6H), 1.22 (m, 20 H), 1.37 (m, 4H), 3.04 (m, 4H), 3.65 (m,

1H, H_4), 3.82 (m, 1H, H_3), 3.88 (m, 1H, H_5), 3.94 (m, 1H, H_2), 4.56 (d, 1H, J = 6.9 Hz, OH_3), 4.70 (d, 1H, J = 4.7 Hz, OH_4), 5.31 (d, 1H, J = 5.2 Hz, OH_2), 5.48 (d, 1H, J = 6.3 Hz, OH_5), 7.56 (t, 1H, J = 5.9 Hz, NH_1), 7.80 (t, 1H, J = 5.9 Hz, NH_6). ^{1}H-NMR (d_6-DMSO, 500 MHz, COSY, 1 drop D_2O added, T = 50°C ppm): δ 0.83 (t, 6H), 1.22 (m, 20 H), 1.37 (m, 4H), 3.04 (m, 4H), 3.65 (dd, 1H, $J_{4,5}$ = 6.2 Hz, $J_{3,4}$ = 3.5 Hz, H_4), 3.82 (t, 1H, $J_{2,3}$ = 3.7 Hz, H_3), 3.88 (d, 1H, H_5), 3.94 (d, 1H, H_2), ^{13}C-NMR (d_6-DMSO, 300 MHz, HMQC, T = 50°C , ppm): 14.65, 22.80, 27.10, 29.47, 29.72, 29.82, 31.98, 38.97, 71.08, 72.37, 73.55, 73.66, 172.70, 173.60, Anal Calcd for $C_{22}H_{44}N_2O_6$: C, 61.08; H, 10.25, N, 6.48. Found: C, 60.94; H, 10.41; N, 6.42.

Example 9

Synthesis of dioctyl D-mannaramide. D-Mannaric acid dilactone (2.14 g, 12.3 mmol) is added to a solution of octylamine (3.10 g, 5.9 mmol) in EtOH (50 ml). After 20 hours stirring the suspension was refluxed for 1 hour and after cooling the precipitate was filtered off and crystallized from EtOH (yield 1.59 g, 3.7 mmol, 30%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 0.87 (t, 6H), 1.25 (m, 20H), 1.42 (m, 4H), 3.08 (m, 4H), 3.70 (t, 2H), 3.88 (t, 2H), 4.79 (d, 2H), 5.41 (d, 2H), 7.87 (d, 2H, NH). ^{13}C-NMR (d_6-DMSO, 300 MHz, ppm): 14.91, 23.05, 27.31, 29.62, 29.99, 32.23, 39.28, 72.05, 72.38, 174.3. Anal Calcd for $C_{22}H_{44}N_2O_6$: C, 61.08; H, 10.25, N, 6.48. Found: C, 60.84; H, 10.39; N, 6.40.

Example 10

Synthesis of dioctyl galactaramide. Diethyl galacterate (2.66 g, 10.0 mmol) was added to a solution of octylamine (2.64 g, 20.5 mmol) in EtOH (50 ml). After 20 hours stirring the precipitate was filtered off and crystallized from DMSO (yield 3.00 g, 6.9 mmol, 69%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 0.90 (bs, 6H), 1.30 (bs, 20H), 1.48 (bs, 4H), 3.14 (bs, 4H), 3.82 (bs, 2H), 4.08 (bs, 2H), 4.17 (bs, 2H), 4.85(bs, 2H), 7.33 (bs, 2H, NH). ^{13}C-NMR (d_6-DMSO, 300 MHz, ppm): 14.11, 22.37, 26.82, 28.95, 29.11, 29.61, 31.60, 38.97,

71.45, 173.34. Anal Calcd for $C_{22}H_{44}N_2O_6$: C, 61.08; H, 10.25, N, 6.48. Found: C, 61.15; H, 10.47; N, 6.44.

Example 11

Synthesis of dicitronellyl D-glucaramide. D-Glucaric acid (lactone) (2.90 g, about 14.0 mmol) was added to a solution of citronellylamine (5.00 g, 32.4 mmol) in EtOH (40 ml). After 20 hours stirring the suspension was refluxed for 3 hours and after cooling the precipitate was filtered off and recrystallized from 2-PrOH. Yield 2.30 g (4.8 mmol, 33%). ^{1}H-NMR (d_6-DMSO, 500 MHz, ppm): δ 0.86 (d, 6H), 1.09-1.45 (m, 10H), 1.58 (s, 6H), 1.66 (s, 6H), 1.95 (m, 4H), 3.12 (m, 4H), 3.71 (bs, 1H), 3.89 (bs, 1H), 3.92 (bs, 1H), 3.98 (bs, 1H), 4.63 (bs, 1H, 4.77 (bs, 1H), 5.10 (t, 2H), 5.35 (bs, 1H), 5.55 (bs, 1H), 7.57 (t, 1H), 7.84 (t, 1H). ^{13}C-NMR (d_6-DMSO, 300 MHz, ppm): 18.45, 20.15, 25.84, 26.44, 30.57, 36.99, 37.09, 37.25, 37.32, 37.53, 71.32, 72.47, 73.89, 74.18, 125.60, 131.37, 172.92, 173.97. Anal Calcd for $C_{26}H_{48}N_2O_6$: C, 64.43; H, 9.98, N, 5.78. Found: C, 64.13; H, 10.02; N, 5.75.

Example 12

Synthesis of didodecyl D-glucaramide. D-Glucaric acid (lactone) (0.81 g, about 3.9 mmol) was added to a solution of dodecylamine (1.94 g, 10.5 mmol) in EtOH (25 ml). After 72 hours stirring the suspension was refluxed for 3 hours and after cooling the precipitate was filtered off and recrystallized from DMSO. Yield 1.30 g (2.4 mmol, 61%). ^{1}H-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): δ 0.89 (t, 6H), 1.29 (m, 36H), 1.47 (t, 4H), 3.13 (m, 4H), 3.75 (m, 1H), 3.92 (m, 1H), 3.97 (m, 1H), 3.99 (m, 1H), 4.50 (bs, 2H), 5.05 (bs, 2H), 7.30 (t, 1H), 7.53 (t, 1H). ^{13}C-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): 14.07, 22.34, 26.79, 28.99, 29.12, 29.33, 31.63, 38.86, 71.15, 72.41, 73.37, 73.55, 172.37, 173.41. Anal Calcd for $C_{30}H_{60}N_2O_6$: C, 66.14; H, 11.10, N, 5.14. Found: C, 66.14; H, 11.05; N, 5.12.

Example 13

Synthesis of didodecyl D-mannaramide. D-Mannaric acid dilactone (0.43 g, 2.5 mmol) was added to a solution of dodeylamine (1.12 g, 6.1 mmol) in EtOH (20 ml). After 72 hours stirring the precipitate was filtered off and crystallized from DMSO (yield 0.35 g, 3.7 mmol, 26%). ^{1}H-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): δ 0.89 (t, 6H), 1.29 (m, 36H), 1.47 (t, 4H), 3.14 (m, 4H), 3.77 (d, 2H), 3.95 (d, 2H), 4.61 (bs, 2H), 5.08 (bs, 2H), 7.54 (t, 1H). ^{13}C-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): 14.05, 22.35, 26.77, 28.98, 29.11, 29.34, 31.63, 38.96, 71.96, 72.31, 173.60. Anal Calcd for $C_{30}H_{60}N_2O_6$: C, 66.14; H, 11.10, N, 5.14. Found: C, 65.76; H, 11.01; N, 5.11.

Example 14

Synthesis of didodecyl galactaramide. Diethyl galacterate (2.66 g, 10.0 mmol) was added to a solution of dodecylamine (3.75 g, 20.5 mmol) in EtOH (50 ml). After 72 hours stirring the precipitate was filtered (yield 4.87 g, 8.9 mmol, 89%). Owing to the low solubility in several solvents tested, no proper NMR spectra could be obtained.

Example 15

Synthesis of dicyclododecyl D-glucaramide. D-Glucaro 6,3-lacton (7.67 g, 40.0 mmol) was added to a solution of cyclododecylamine (14.93 g, 81.6 mmol) in 2-methoxyethanol (125 ml). The reaction mixture was heated slowly till T = 120° C in 3h and kept at this T for 4 hours. After cooling the precipitate was filtered off and recrystallized from DMSO and EtOH . Yield 9.50 g (17.6 mmol, 44%). ^{1}H-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): δ 1.36 (m, 36H), 1.60 (m, 4H), 3.75 (m, 1H), 3.97 (m, 5H), 4.47 (bs, 2H), 6.98 (bs, 1H), 7.21 (bs, 1H). ^{13}C-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): 22.03, 23.97, 24.14, 30.59, 45.45, 71.21, 72.32, 73.33, 73.71, 171.76, 172.76. Anal Calcd for $C_{30}H_{56}N_2O_6$: C, 66.63; H, 10.44, N, 5.18. Found: C, 67.00; H, 11.30; N, 4.97.

Example 16

Synthesis of dicyclododecyl D-mannaramide. D-Mannaric acid dilactone (1.99 g, 11.4 mmol) was added to a solution of cyclododecylamine (0.58 g, 5.9 mmol) in EtOH (20 ml). After 20 hours stirring the solution was refluxed for 2 hours and after cooling the precipitate was filtered off and crystallized from EtOH and DMSO (yield 0.51 g, 0.94 mmol, 10%). ^{1}H-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): δ 1.36 (m, 36H), 1.61 (m, 8H), 3.75 (bs, 2H), 3.93 (bs, 4H), 4.58 (bs, 2H), 5.07 (bs, 2H), 7.24 (d, 2H, NH). ^{13}C-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): 22.05, 23.99, 24.17, 30.62, 45.68, 72.23, 173.01. Anal Calcd for $C_{30}H_{56}N_2O_6$.0.25 C_2H_6SO: C, 65.01; H, 10.46, N, 5.05 Found: C, 65.08; H, 10.29; N, 5.05.

Example 17

Synthesis of dicyclododecyl galactaramide. Diethyl galacterate (2.67 g, 10.0 mmol) was added to a solution of cyclododecylamine (3.78 g, 20.7 mmol) in EtOH (50 ml). After 48 hours stirring the precipitate was filtered and washed with H_2O and EtOH (yield 2.43 g, 4.5 mmol, 45%). Owing to the low solubility in several solvents tested, no proper NMR spectra could be obtained.

Example 18

Synthesis of di-8-pentadecyl D-glucaramide. D-Glucaric acid (lactone) (2.53 g, about 12.7 mmol) is added to a solution of 8-aminopentadecane (5.17 g, 26.1 mmol) in EtOH (35 ml). After 20 hours stirring the suspension was refluxed for 20 hours and recrystallized from EtOH/H_2O (3x). Yield 0.72 g (1.3 mmol, 10%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 0.86 (t, 12H), 1.23 (m, 32H), 1.36 (t, 8H), 3.69 (bs, 3H), 3.88 (bs, 1H), 3.94 (bs, 1H), 3.99 (m, 1H), 4.56 (bs, 1H), 4.71 (bs, 1H), 5.33 (bs, 1H), 5.47 (bs, 1H), 7.15 (d, 1H), 7.41 (d, 1H). ^{13}C-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): 14.86, 23.03, 26.37, 29.58, 29.68, 32.21, 35.36, 48.78, 48.97, 71.43, 71.73, 73.85,

74.30, 172.52, 173.71. Anal Calcd for $C_{30}H_{60}N_2O_6$: C, 67.09; H, 11.26, N, 4.89. Found: C, 66.98; H, 11.38; N, 4.90.

Example 19

Synthesis of dioleyl D-glucaramide. D-Glucaric acid (lactone) (1.27 g, about 6.5 mmol) was added to a solution of oleylamine (3.87 g, 14.4 mmol) in EtOH (30 ml). After 20 hours stirring the suspension was refluxed for 0.5 hour and recrystallized from EtOH (2x) and DMSO. Yield 0.72 g (1.4 mmol, 21%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 0.88 (t, 6H), 1.28 (m, 44H), 1.45 (m, 4H), 2.01 (m, 8H), 3.07 (bs, HDO + 4H), 3.75 (m, 1H), 3.91 (m, 1H), 3.96 (m, 1H), 3.98 (m, 1H), 4.38 (bs, 1H), 4.52 (bs, 1H), 5.10 (bs, 2H), 5.35 (m, 4H), 7.32 (bs, 1H), 7.55 (bs, 1H). ^{13}C-NMR (d_6-DMSO, 500 MHz, T = 100° C, ppm): 14.36, 22.61, 27.04, 27.30, 27.34, 29.24, 28.28, 29.38, 29.44, 29.48, 29.62, 29.68, 29.76, 29.80, 31.88, 39.12, 39.20, 71.40, 72.67, 73.67, 73.86, 130.3, 172.68, 173.68. Anal Calcd for $C_{42}H_{80}N_2O_6$: C, 71.14; H, 11.37, N, 3.95. Found: C, 70.87; H, 11.43; N, 3.97.

Example 20

Synthesis of 3-*O*-methyl-dicyclohexyl D-glucaramide. 3-*O*-Methyl diethyl D-glucarate (0.54 g, 1.9 mmol) was added to a solution of cyclohexylamine (0.48 g, 4.8 mmol) in EtOH (20 ml). After 20 hours stirring the precipitate was filtered off. Yield 0.20 g (0.75 mmol, 39%). ^{1}H-NMR (d_6-DMSO, 300 MHz, ppm): δ 1.26 (m, 10H), 1.70 (m, 10H), 3.32 (s, 3H), 3.59 (m, 2H), 3.65(m, 1H), 3.74 (m, 1H), 3.89 (m, 1H), 4.08 (m, 1H), 4.78 (m, 1H), 5.45 (bs, 2H), 7.40 (d, 1H), 7.51 (d, 1H). ^{13}C-NMR (d_6-DMSO, 300 MHz, ppm): 24.53, 26.13, 33.21, 48.20, 60.95, 72.35, 73.24, 74.51, 81.85, 172.00, 172.50. Anal Calcd for $C_{19}H_{34}N_2O_6$: C, 59.05; H, 8.87, N, 7.25. Found: C, 58.91; H, 8.90; N, 7.27.

Example 21

Synthesis of 3-*O*-methyl-didodecyl D-glucaramide. 3-O-Methyl diethyl D-glucarate (0.60 g, 2.1 mmol) was added to a solution of cyclododecylamine (0.93 g, 5.0 mmol) in EtOH (20 ml). After 72 hours stirring the precipitate was filtered off and crystallized from EtOH. Yield 0.55 g (0.98 mmol, 46%). ^{1}H-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): δ 0.84 (t, 6H), 1.26 (m, 36 H), 1.45 (m, 4H), 3.34 (s, 3H), 3.70 (m, 1H), 3.80 (m, 1H), 3.95 (m, 1H), 4.09 (m, 1H), 4.58 (bs, 1H), 5.03 (bs, 2H), 7.32 (bs, 1H), 7.42 (bs, 1H). ^{13}C-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): 14.08, 22.38, 26.83, 29.03, 29.16, 28.38, 31.66, 38.97, 60.02, 72.06, 72.72, 73.91, 81.39, 172.37, 173.15. Anal Calcd for $C_{31}H_{62}N_2O_6$: C, 66.63; H, 11.18, N, 5.01. Found: C, 66.63; H, 11.33; N, 5.04.

Example 22

Synthesis of 3-*O*-methyl-dicyclododecyl D-glucaramide. 3-*O*-Methyl diethyl D-glucarate (0.60 g, 2.1 mmol) is added to a solution of cyclododecylamine (0.98 g, 5.3 mmol) in EtOH (20 ml). After 20 hours stirring the precipitate was filtered off and crystallized from EtOH. Yield 0.30 g (0.54 mmol, 25%). ^{1}H-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): δ 1.33 (m, 36H), 1.57 (m, 8H), 3.35 (s, 3H), 3.69 (bs, 1H), 3.77 (bs, 1H), 3.93 (bs, 3H), 4.09 (bs, 1H), 4.47 (bs, 1H), 5.03 (bs, 2H), 7.02 (d, 1H), 7.12 (d, 1H). ^{13}C-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): 22.02, 23.97, 24.16, 30.61, 45.52, 60.06, 71.91, 72.62, 72,76, 73.86, 81.43, 171.71, 172.42. Anal Calcd for $C_{31}H_{58}N_2O_6$: C, 67.11; H, 10.54, N, 5.05. Found: C, 65.64; H, 10.44; N, 5.00.

Example 23

Synthesis of N_1-cyclododecyl, N_6-cyclohexyl D-glucaramide. Cyclohexylammonium 6-(N-cyclohexyl)-D-glucaramide-1-ate (0.60 g, 2.1 mmol) was added to a solution of Dowex H^+ (1x8) in H_2O (40 ml). After 30 minutes stirring the suspension is filtered and washed thoroughly with H_2O. The

filtrate was evaporated and the crude 6-(N-cyclohexyl)-D-glucaramide (lacton) was added to a solution of p-toluene sulfonic acid (0.038 g, 0.20 mmol) in EtOH (20 ml). At T = 50°C cyclododecylamine (0.47 g, 2.6 mmol) was dropped slowly to the solotion. After 1 h stirring the solution was cooled to T = 4°C and recrystallized from DMSO/H_2O. Yield 0.13 g (0.33 mmol, 13%). ^{1}H-NMR (d_6-DMSO, 300 MHz, T = 100° C, ppm): 1.13-1.75 (m, 32 H), 3.59 (bs, 1H), 3.70 (m, 1H), 3.92 (m, 1H), 3.94 (m, 2H), 3.99 (m, 1H), 4.49 (bs, 1H), 4.63 (bs, 1H), 5.20 (bs, 1H), 5.33 (bs, 1H), 7.13 (bs, 1H), 7.45 (bs, 1H).). ^{13}C-NMR (d_6-DMSO, 300 MHz, T = 95° C, ppm): 22.20, 22.27, 24.20, 24.38, 25.05, 25.89, 30.86, 32.80, 32.84, 45.65, 48.15, 71.41, 72.68, 73.65, 73.90, 172.05, 172.80.

Example 24 Solvent scope of N,N'-dialkylaldaramides (1%) or N,N'-dialkylpentaramides (1%) 1-24 refers to the compounds prepared in example 1-23)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Hexadecane	ns	Ns	ns	ns	ns	-	ns	ns	ns	ns	p	ns	ns	ns	ns	ns	ns	s	p	ns	p	ns	-
Cyclohexane	ns	Ns	ns	ns	G	ns	ns	ns	ns	ns	g*	ns	ns	ns	g	ns	ns	s	p	ns	g	g	p
p-xylene	ns	Ns	ns	p	G	-	ns	ns	ns	ns	p	ns	ns	ns	g	ns	ns	s	p	p	p	p	p
Toluene	ns	Ns	ns	p	G	ns	ns	ns	ns	ns	p	ns	ns	ns	g	ns	ns	s	p	p	p	p	-
n-butylacetate	ns	Ns	ns	p	G	ns	ns	ns	ns	ns	p	ns	ns	ns	g	ns	ns	s	c	p	c	p	p
1,2-dichloroethane	ns	Ns	ns	s	cg	p	ns	ns	ns	ns	s	p	c	ns	g	c	ns	s	c	c	p	p	-
2-octanol	P	Ns	ns	p	cg	-	ns	ns	ns	ns	s	ns	p	ns	s	s	ns	s	c	p	c	p	-
2-propanol	C	C	c	p	cg	-	c	c	c	ns	s	ns	c	ns	c	cg	ns	s	c	c	p	p	-
Ethanol	C	C	c	s	cg	-	c	c	c	c	s	p	ns	ns	cg	p	ns	s	c	c	p	p	-
Dimethylsulfoxide	S	C	s	s	cg	-	c	s	c	s	s	s	c	ns	cg	p	ns	s	c	s	p	p	-
Water	ns	Ns	ns	ns	ns	-	ns	ns	ns	ns	c	ns	ns	ns	ns	ns	ns	p	ns	ns	ns		-
silicon oil	-	-	-	-	G	-	-	-	-	-	-	-	-	-	g	-	ns	s	-	-	v	-	v
methyl laurate	-	-	-	-	G	-	-	-	-	-	-	-	-	-	g	-	ns	s	-	-	-	-	p
methyl benzoic acid	-	-	-	-	S	-	-	-	-	-	-	-	-	-	g	-	ns	s	-	-	p	-	p
2-methoxyethanol	-	-	-	-	S	-	-	-	-	-	-	-	-	-	c	-	ns	s	-	-	-	-	p

g = gelation, s = soluble, p = precipitates, c = crystallizes, ns = not soluble, v = viscous, g* = unstable gel, precipitates , cg = crystalline gel

Example 25 Gelation of N,N'-dialkylaldaramides (1%) in mixtures of solvents

	11 (cit-Glu-cit)	12 (12-Glu-12)	15 (C12-Glu-C12)
cyclohexane	g*	ns	g
cyclohexane/dioxane 1:1	s	-	cg
Dioxane	s	c	cg
dioxane/H_2O 3:1	s	c	cg
dioxane/H_2O 2:1	s	c	cg
dioxane/H_2O 1:1	p	ns	g
dioxane/H_2O 1:2	p	ns	ns
H_2O	c	ns	ns

g = gelation, s = soluble, p = precipitates, c = crystallizes, ns = not soluble, g* = unstable gel, precipitates , cg = crystalline gel

Example 26

Addition of a solution of the gelling agent (10% in NMP, 0.05 ml) to an organic solution (0.5 ml, "cold gelation")

	5 (C6-Glu-C6)	12 (12-Glu-12)	15 (C12-Glu-C12)	18 (B13-Glu-B13)
cyclohexane	p	p	g	s
methyllaurate	c	p	g	s
Toluene	c	p	g	s
n-butyl acetate	c	p	g	s
1,2-dichloroethane	c	p	c	s
silicon oil	-	-	g	-
Aceton	-	-	cg	-
benzaldehyde	-	-	s	-
Chloroform	-	-	s	-
diethylether	-	-	g	-
ethylacetate	-	-	p	-
Heptane	-	-	p	-
Hexane	-	-	p	-
Acetonitril	-	-	g	-
tetrahydrofuran	-	-	c	-

Example 27

Maximum gelator concentration of 5 (C6-Glu-C6) and 15 (C12-Glu-C12)

	5 (in %) (C6-Glu-C6)	15 (in %) (C12-Glu-C12)
cyclohexane	< 5	< 5
methyllaurate	< 2.5	< 5
silicon oil (Dow Corning 702)	< 2.5	< 50
Toluene	< 2.5	< 50
n-butylacetate	< 2.5	< 50
1,2-dichloroethane	< 5	< 50

Example 28

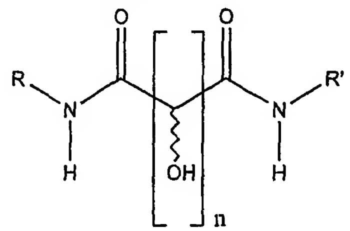
Phase diagram of 5 (C6-Glu-C6) and 15 (C12-Glu-C12) (dropping ball method)

The phase diagram of 5 (C6-Glu-C6) and 15 (C12-Glu-C12) was determined (see Figure 1) by using the dropping ball method (A. Takashi, M. Sakai, T. Kato, *Polym. J.*, 12 (1980) 335-341, F.S. Schoonbeek, J.H. van Esch, R. Hulst, R.M. Kellogg, B.L. Feringa, *Chem. Eur. J.*, 6 (2000) 2633-2643). A linear correlation was observed between the T_m^{-1} and the logarithm of the mole fraction of 15 (C12-Glu-C12) in cyclohexane, silicon oil and p-xylene, as expected for the dissolution proces of crystals (gels) (K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, S. Shinkai, *J. Am. Chem. Soc.*, 116 (1994) 6664-6676).

Claims

1. A gelling agent or thickener in the form of a N,N'-disubstituted aldaramide, a N,N'-disubstituted pentaramide, or a derivative thereof.

2. A gelling agent or thickener according to claim 1 having the formula



(I),

wherein n is 3 or 4, and wherein R and R' represent the same or different substituents chosen from the group of substituted or unsubstituted, branched, possibly aromatic groups containing, cyclic or linear alkyl, alkenyl, alkynyl groups having from 1 to 40 carbon atoms.

3. A gelling agent or thickener according to claim 2, wherein R and R' , R and R' each represent independently a linear, branched, or cyclic alkyl group having 4-20 carbon atoms.

4. A gelling agent or thickener according to claim 3, wherein R and R' each are independently selected from the group of cycloalkyl groups having 4-16 carbon atoms.

5. A gelling agent or thickener according to any of the claims 2-4 wherein R and R' are the same.

6. A gelling agent or thickener according to any of the preceding claims being a N,N'-dicycloalkyl deglucaramide.

7. A process for preparing a gelling agent or thickener according to any of the preceding claims, comprising oxidation of an aldose or pentose to form an aldaric or pentaric acid or a salt thereof, and condensation with a primary amine of the formula RNH_2 and a primary amine of the formula $R'NH_2$.

8. A process according to claim 7, wherein the aldaric or pentaric acid or salt thereof is activated before condensation by lactonization and/or esterification.

9. A process according to any claim 7 or 8 wherein the aldose or pentose is chosen from the group of allose, altrose, glucose, mannose, gulose, idose, galactose, talose, ribose, arabinose, xylose, lyxose and derivatives thereof.

10. A process according to claim 9, wherein the derivative is a deoxy aldose or pentose, an ether, or an ester

11. A process for preparing a gel or thickening by mixing a gelling agent or thickener according to any one of claims 1-6 with a composition.

12. A process according to claim 11 wherein the composition comprises an organic solvent.

13. A process according to claim 12 wherein the solvent is chosen from the group of aromatic and non-aromatic hydrocarbons, alcohols, ethers, esters, aldehydes, alkanoic acids, epoxides, amines, halogenated hydrocarbons, silicon oils, vegetable oils, phosphoric esters, sulfoxides, water and mixtures thereof.

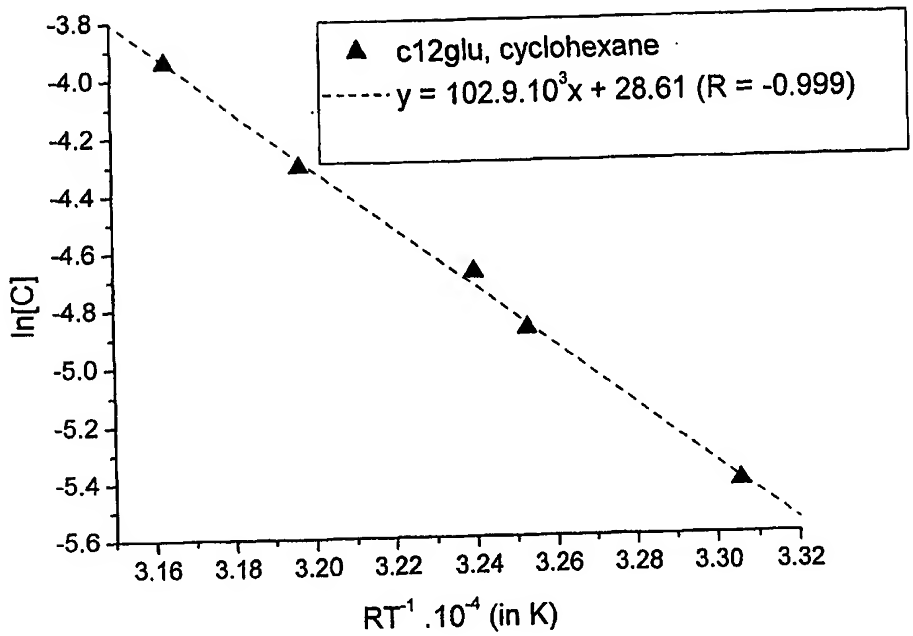
14. A process according to any one of claims 11-13 wherein the gelling agent or thickener is mixed with the composition in a ratio of between 0.01 and 50% by weight.

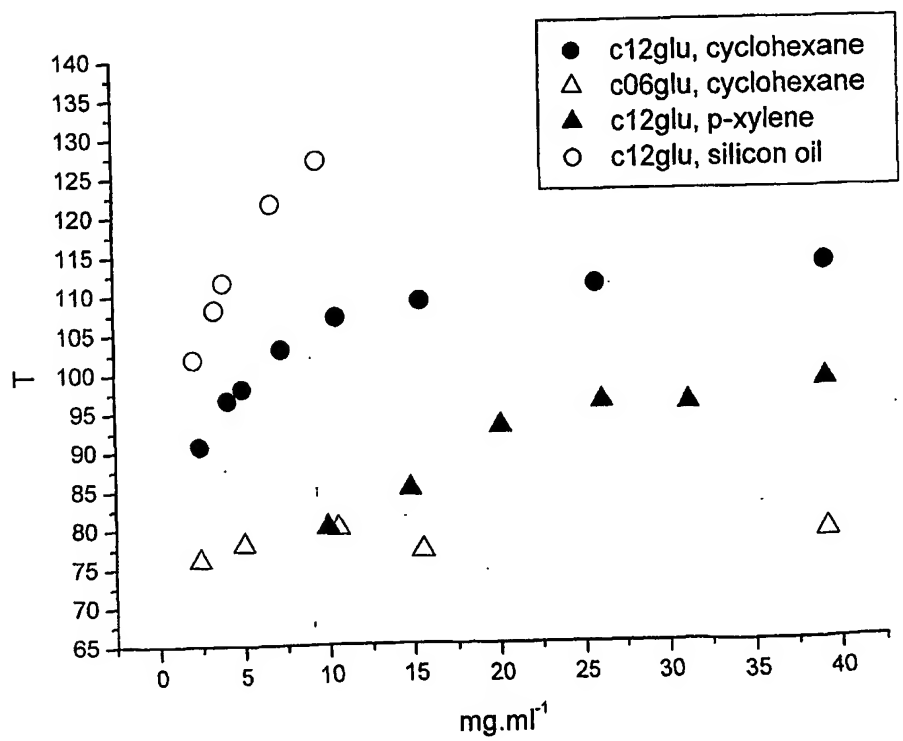
15. A process according to any one of claims 13-14 wherein the mixture of the gelling agent or thickener and the composition is heated, or wherein a solution of the gelling agent or thickener is added to or sprayed into the composition.

16. A gel comprising a gelling agent or thickener according to any one of claims 1-6.

17. A gel according to claim 16 obtainable by a process according to any one of claims 11-15.

Fig. 1


c12glu, cyclohexane
y = 102.9.10³x + 28.61 (R = -0.999)
ln[C]
-3.8
-4.0
-4.2
-4.4
-4.6
-4.8
-5.0
-5.2
-5.4
-5.6
3.16
3.18
3.20
3.22
3.24
3.26
3.28
3.30
3.32
RT⁻¹ .10⁻⁴ (in K)


c12glu, cyclohexane
c06glu, cyclohexane
c12glu, p-xylene
c12glu, silicon oil
T
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
0
5
10
15
20
25
30
35
40
mg.ml⁻¹

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 02/00151

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C235/06 C07C235/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, EPO-Internal, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	A. C. KURTZ ET AL: "Saccharolactone as a reagent for precipitating cartain amines" J. BIOL. CHEM., 1939, pages 693-99, XP001013068 cited in the application table I	1-3,5-9
X	P. D. HOAGLAND: "The Formation of Intermediate Lactones During Aminolysis of Diethyl Galactarate" CARBOHYDRATE RES., vol. 98, 1981, pages 203-8, XP001013051 cited in the application page 207, line 6 page 207, line 30 -page 208, line 6	1-3,5-9

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 April 2002	24/04/2002

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 478 374 A (KIELY, DONALD E.) 26 December 1995 (1995-12-26) * table 1, last three examples, column 1, lines 38-42 * ---	1-3,5
X	CHEMICAL ABSTRACTS, vol. 114, no. 1, 7 January 1991 (1991-01-07) Columbus, Ohio, US; abstract no. 7009, CHEN, L. ET AL: "Molecular modeling of acyclic carbohydrate derivatives N,N'-dimethyl- and N,N'-dihexylxylaramide. Model compounds for synthetic poly(hexamethylenexylaramide)" XP002173886 * abstract and RN 130741-88-7 * abstract & ACS SYMP. SER. (1990), 430(COMPUT. MODEL. CARBOHYDR. MOL.), 141-51, 1990, ---	1-3,5
X	US 2 084 626 A (TABERN DONALEE L) 22 June 1937 (1937-06-22) examples 1,3,4 ---	1,2,5-9
X	DATABASE BEILSTEIN 'Online! BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT/MAIN, DE; Database accession no. 6247081 (BRN) XP002173887 abstract & K. REHSE ET AL.: ARCH. PHARM., vol. 320, no. 11, 1987, pages 1155-61, ---	1,2,5
X	DATABASE BEILSTEIN 'Online! BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT/MAIN, DE; Database accession no. 3222706 (BRN) XP002173888 abstract & J. PRAKT. CHEM. <2>6, 1872, page 141 ---	1,6-9
X	DATABASE BEILSTEIN 'Online! BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT/MAIN, DE; Database accession no. 1729539 (BRN) XP002173889 abstract & J. CHEM. SOC., 1957, page 805, 809 --- -/--	1,2,5-9

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE BEILSTEIN 'Online! BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT/MAIN, DE; Database accession no. 1668843 (BRN) XP002173890 abstract & YAKUGAKU ZASSHI, 86, 1966, page 1057, 1062 ---	1
X	DATABASE BEILSTEIN 'Online! BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT/MAIN, DE; Database accession no. 40270 (BRN) XP002173891 abstract & J. AMER. CHEM. SOC., vol. 71, 1949, page 4131 ---	1,6-9
X	DATABASE BEILSTEIN 'Online! BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT/MAIN, DE; Database accession no. 3226566 (BRN) XP002173892 abstract & BULL. CHEM. SOC. CHIM. FR. <2> 48,, 1887, page 721 ---	1,6-9
X	GB 781 255 A (GEIGY AG J R) 14 August 1957 (1957-08-14) * table page 2, examples 2 und 6 * ---	1,6-9
A	US 5 112 601 A (SEBAG HENRI ET AL) 12 May 1992 (1992-05-12) page 1, line 5 - line 37; claims ----	1-16

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

With regard to the very general expression "derivatives of aldaramide and pentaramide" the scope of claim 1 is considered unclear to such an extend that a complete search is not possible. The search has therefore be limited to compounds having the structure (I) of claim 2. However, despite this limitation the search revealed a very large number of documents relevant to the issue of novelty, which cannot possibly be cited. Search and search report can be considered complete for compounds of formula (I) wherein R and R' are unsubstituted linear, branched or cyclic alkyl groups having 4-20 carbon atoms (claims 3, 4 and 6). The documents cited against claims 1 and 2 are merely an arbitrary selection of the large number of novelty destroying documents.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Ir   ional Application No
I'C'/NL 02/00151

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5478374	A	26-12-1995	US	5329044 A	12-07-1994
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			GB	2231871 A ,B	28-11-1990
			US	5247121 A	21-09-1993